

MONITORING OF POTENTIAL OCCUPATIONAL EXPOSURES
OF MIXERS/LOADERS AND PILOTS
DURING APPLICATION OF PHOSDRIN (MEVINPHOS)
IN MONTEREY COUNTY IN 1981

By

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SUMMARY

Potential inhalation and dermal exposure of mixer/loaders and pilots to Phosdrin (mevinphos) during helicopter applications were measured in Monterey County during March 1981. One aerial pest control operator firm was monitored for a period of 3 days. The amount of Phosdrin on each worker's skin and in the breathing zone was monitored for 1.13 to 2.80 hours. Using these results, estimates were made of each worker's potential total exposure during a 7-hour workday. It was estimated that mixer/loaders were exposed to levels of Phosdrin that ranged from 320 to 8,059 micrograms, with a mean of 3,107; pilots were exposed to levels ranging from 78 to 239 micrograms, with a mean of 166. Comparing these exposure levels, assuming Phosdrin is 100 percent absorbed through the exposed skin of a worker, and accepting a no-observed-effect level (NOEL) of 0.014 mg/kg/ day for Phosdrin in humans (Rider, et al, 1975), it appears that exposures of mixer/loaders and pilots observing California Department of Food and Agriculture safe use regulations can be contained to levels which do not exceed this value.

INTRODUCTION

In 1980, in the State of California, 14,693 applications of Phosdrin (mevinphos) were made to more than 524,903 acres of various crops, using 306,066 pounds of active ingredient (California Department of Food and Agriculture, 1981).

Phosdrin is one of the most toxic organophosphate chemicals used in California agriculture. Symptoms of Phosdrin poisoning, in common with other anticholinesterase agents, include headache, nausea, dizziness, sweating, weakness, ataxia, miosis, and muscle twitching.

Durham and Wolfe (1962) and Wolfe (1967) made measurements of air concentration levels for inhalation exposure and the levels of concentration on cloth patches at various body sites for dermal exposure, and calculated the total amount of various organophosphate pesticides that an individual worker might be exposed to; these authors' studies did not include Phosdrin. It was proposed to study the inhalation and dermal exposure potential of mixer/loaders and agricultural pilots during aerial applications of phosdrin during March 1981 in Monterey County.

MATERIALS AND METHODS

The cooperating aerial application firm selected for this study is located in Monterey County, and is a major pesticide applicator. This firm has an excellent record of compliance with established safe use regulations and work practices. All mixing, loading, and application procedures were performed in compliance with the Department's pesticide regulations, including using licensed pilots, providing clean coveralls daily, providing medical supervision with blood testing for cholinesterase levels, and using mechanical closed systems for mixing and loading.

Helicopters were used exclusively in this study. Helicopters carry smaller loads than conventional airplanes utilized in pesticide applications, and are reloaded much more often. Reloading took place every 5-7 minutes during the study.

The closed system that was utilized contained a manually operated probe which was placed into the proper opening of the pesticide container. A pump was used to draw the pesticide out of the container into the mix tank. Spray adjuvants and other pesticides were added to the mix tank when necessary. Contents of the mix tank were diluted with water to the desired concentration, using an inlet valve, and were pumped into the helicopter. The exit end of the loading hose was equipped with an automatic shut-off coupler to prevent spillage.

The mixer/loaders in this study wore shirts and pants under clean long-sleeved and long-legged cloth coveralls, heavy rubber gloves, and rubber boots. Respirators were worn by all workers with the exception of the pilot on day 2.

The pilots had no role in mixing or loading procedures, but did, on occasion, assist in the cleanup of their aircraft. An exception did occur on day 1 when the pilot assisted in the repair of a substantial leak in the plumbing of the closed system. Sampling gear had not been placed on the pilot at this time. Exposure to the hands was large in this incident (878 micrograms found in the preapplication handwash), suggesting that actual handwash data for this exposure did not represent a "normal" application. As a result, hand exposure for this worker was calculated by taking the average of the other two pilots' exposure.

Monitoring periods were selected when at least 1 hour of continuous aerial application was expected to occur. Typical applications took place in the morning, and lasted 1 to 3 hours.

No attempt was made to measure oral ingestion exposure. Potential inhalation exposure outside the respirator was measured by placing an MSA Model S portable air pump (at a flow rate of 1 cubic liter of air per minute) on each worker. The air intake hose was attached to the clothing under the chin area. Air sampling tubes containing Amberlite XAD-4 resin were inserted in the tygon air intake line.

Potential exposure to exposed skin area and skin protected by cotton coveralls was measured with patches made of an outer layer of 7-ounce 65% Dacron Polyester, 35% cotton twill, and an inner layer of 100% cotton gauze backed by aluminum foil. Each patch contained a premarked area of 49 cm² which could be cut out and analyzed. A single patch was placed on the back of the neck, on each upper arm, on each thigh, and on each side of the chest. Pre- and post-application handwash samples were taken by rinsing the workers' hands in approximately 250 ml of distilled water.

At the conclusion of each application, the air sampling tubes and handwash samples were placed on ice in individual glass jars sealed with aluminum foil. The patches were removed from the clothing, the taped edges were cut off, and each gauze and outer cloth patch were carefully separated. Matched pairs of patches were placed together in glass jars (i.e., outside cloth of left and right arms were combined, as were inside gauze and foil from left and right thighs). All samples were shipped in iced containers by air freight to Sacramento, and were received by the laboratory within 24 hours.

RESULTS

The results of the various experimental data and information are summarized in the following tables:

Table 1 - Air concentration levels monitored for inhalation exposure of various workers. Daily inhalation exposure₃ (Column 3) was estimated by assuming an air inhalation volume of 1.25 m³/hour and 100 percent absorption by the lung.

Tables 2 and 3 - The dermal exposure of workers determined by sampling patches. Column A is the sampling period. Column B is the results of

Phosdrin exposure in micrograms per square centimeter. Column C is an estimate of the Phosdrin exposure in square centimeters adjusted for a typical full day's exposure. Column D is an estimate of the average area of the skin of each body part in square centimeters, according to Berkow (1931) and DuBois and DuBois (1916). This assumes an average person, weighing 70 kg and standing 175 cm. Column E is an estimate of the dermal exposure to Phosdrin in micrograms per day to each body part. The calculations for the anterior portions of the head and neck use a combination of Phosdrin residues on the outside cloth and inside gauze samples placed on the chest to represent exposure of bare skin to airborne Phosdrin. (This assumes no face protection from respirator or shield, although all mixer/loaders and 2 of the 3 pilots monitored wore respirators.) Calculations for the posterior portion of the head and neck use a combination of the Phosdrin residues on the outside cloth and inside gauze sample placed on the back of the neck. Calculations for the anterior and posterior portions of the trunk use the gauze portions of the samples taken on the chest and back of the neck respectively. Similarly, the calculations for the arms and forearms use the gauze portion of the samples taken on the upper arms; the anterior legs and feet use the gauze portion of the samples taken on the thighs. Calculations for the posterior portion of the legs are derived by multiplying the back of neck/chest ratio by the thigh concentration. This is done after assuming that anterior and posterior exposures may differ, and that the back of neck to chest concentration ratio approximates the ratio of posterior to anterior leg concentration. Column F is the sum of the dermal exposure to the body parts, excluding the hands.

Table 4 - The dermal exposure of workers' hands using handwash sampling. Column A is the sampling period. Column B is the amount of Phosdrin found in the sample. Column C is the amount of Phosdrin estimated to be on the workers' hands at the end of a normal 7-hour workday.

Table 5 - Total of dermal and inhalation exposures during a full day's (7-hour) work with Phosdrin.

Appendix 1 - Use pattern data and information during aerial application of Phosdrin.

Appendix 2 - Description of calculations used in Tables 2-4.

Appendix 3 - Description of Phosdrin extraction and analysis procedures.

DISCUSSION

Applications were monitored exactly as they were being done rather than set up an "ideal" study with more control of variables. The cooperating firm was subject to California work practices and regulations that should have resulted in less exposure than would be typical in other states in the United States. For example, the required use of clean outer coveralls daily and the closed system for mixing and loading of Phosdrin would be expected to reduce daily inhalation and dermal exposure of workers as it has for other pesticides studied. The inhalation exposure, in micrograms

per cubic meter of air, was found to be at levels ranging from 2.4 to 4.5 for mixer/loaders, and from 0.9 to 2.2 for pilots.

In order to simulate whole body dermal exposure due to the penetration through the coveralls, cloth pads were designed with 3 layers of material. The outer layer was coverall material; next there was a layer consisting of heavy cotton gauze; the final layer was aluminum foil. The amount that penetrated the top layer and became entrapped in the gauze was considered as the amount that might penetrate the coveralls and reach the skin.

A legend explaining the method of calculations used in Tables 2 and 3 is found in Appendix 2. The most extreme dermal exposure situation is when no clothing is worn under a worker's coveralls; sometimes varying amounts of clothing are worn under the coveralls.

The major route of Phosdrin exposure appears to be dermal. Dermal values of mixer/loaders (excluding hand exposure) ranged from a low of 202 to a high of 4,653 micrograms; pilots were exposed to levels ranging from 24 to 84 micrograms. Exposure of hands, measured by handwash samples, in micrograms per 7-hour workday, ranged from 97 to 3,383 for mixer/loaders, and from 42 to 136 for pilots.

The oral LD₅₀ for phosdrin has been reported to be 3.7 mg/kg, and dermal LD₅₀ has been reported to be 4.2 mg/kg (University of California, 1979). We estimate the dermal transport rate as 3.7 mg/kg/4.2 mg/kg, or 88 percent. As this value approximates 100 percent, we will use 100 percent as a "worst case" value for dermal transport.

Rider (1975) reported that no effects were seen with humans ingesting 1 mg Phosdrin per day for a period of 30 days. Assuming a weight of 70 kg for the average worker, this value corresponds to a NOEL of 0.014 mg/kg/day. On the basis of the 100 percent dermal absorption rate, we assume that the dermal toxicity of Phosdrin is approximately equivalent to its oral toxicity. Therefore, we will use the value of 0.014 mg/kg/day to represent the human NOEL for Phosdrin.

More extensive toxicity data exists for other test species. Lewis (1972) reported no somatic symptoms in monkeys and pigeons at doses of 0.15 mg/kg and 0.35 mg/kg respectively. Mertens (1975) found no behavioral performance deficits or overt somatic signs in gerbils receiving Phosdrin doses of 0.10 mg/kg.

CONCLUSION

The exposure of pilots to Phosdrin in this study does not seem to be significant in terms of potential adverse health effects. The highest estimated total exposure, 239 micrograms, corresponds to a level of 0.003 mg/kg/day for a 70 kg worker. This level seems to be safely below the NOEL of 0.014 mg/kg/day.

The estimated potential exposure of the mixer/loader (day 3) of 8,059 micrograms, corresponding to 0.117 mg/kg/day, exceeds the established no observable effect level. In this exposure, however, we found an abnormally high preexposure handwash concentration (123 micrograms), suggesting contamination of the gloves prior to the application. Observations of the actual application revealed that the mixer/loader often removed his gloves when reaching into the pocket of his coveralls, and also often touched the thigh patches while wearing the gloves, resulting in high anterior leg concentration (2,636 micrograms). While we cannot ignore this high concentration, we conclude that it does not reflect normal application conditions. It should be noted that no apparent somatic symptoms were evident during this exposure.

The second highest mixer/loader concentration of 943 micrograms, corresponding to 0.014 mg/kg/day for a 70 kg worker, equals the NOEL for Phosdrin. It should be noted that estimates of total exposure are for a 7-hour workday, and that the NOEL was derived from a study in which volunteers received Phosdrin daily for 30 consecutive days. Actual applications do not often last for periods of 7 hours or more, and even in heavy use periods, it seems unlikely that workers would make Phosdrin applications daily for periods approaching 30 consecutive days. It appears, therefore, from the standpoint of acute toxicity, that exposures of mixer/loaders and pilots during helicopter applications can be kept to safe levels when obeying required California Department of Food and Agriculture safety procedures.

Previous measurements of Phosdrin exposure of mixers and loaders handling liquid formulations in California, and the same kind of workers handling similar organophosphates in California and other states, indicate that casual handling of such pesticides can result in potential exposure of 100 to 500 milligrams per person per day as compared to workers in this study, with potential maximum exposure in the 1 to 8 milligram exposure range. The very low exposure potential is primarily the result of careful work practices and the careful use of closed mixing and loading systems that allow the use of highly toxic products without the need for bulky impervious protective clothing.

Before application firms began using closed system equipment 6 years ago, severely depressed cholinesterase values and serious poisonings were common events.

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Table 1

Amount of Phosdrin Found in the Breathing Zone
of Mixer/Loaders and Pilots

Worker	Column 1	Column 2	Column 3
	PPB (V.V.)	Mg/m ³	Estimated Daily Inhalation Exposure for 7-Hour Day (Micrograms) If a Respirator Not Worn
Mixer/Loader, Day 1	0.5	4.5	39
Mixer/Loader, Day 2	0.1	1.0	9
Mixer/Loader, Day 3	0.3	2.4	21
Pilot, Day 1	0.2	2.2	19
Pilot, Day 2	0.3	2.5	22
Pilot, Day 3	0.1	0.9	8

Table 2

Dermal Phosdrin Exposure
to Mixer/Loaders (Excluding Hands)

Worker	Column A Skin Area Studied	Column B Hours of Exposure	Column C Amount of Phosdrin on Cloth Pads (mg/cm ²) Outside Inside Cloth Gauze	Column D Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²) Outside Inside Cloth Gauze	Column E Area of Skin Surface Covered Bare Skin (cm ²) Covered Bare Skin	Column F Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms) Covered Bare Skin	Column G Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
Mixer/ Loader Day 1	Face and Head, Anterior	2.8	0.16 0.005	0.40 0.013	- 650	- 268	-
	Neck, Anterior	2.8	0.16 0.005	0.40 0.013	- 160	- 66	-
	Head and Neck, Posterior	2.8	0.027 ND	0.068 ND	- 300	- 20	-
	Trunk, Anterior	2.8	0.16 0.005	0.40 0.013	3,700	48	-
	Trunk, Posterior	2.8	0.027 ND	0.068 ND	3,330	ND	-
	Arms and Forearms	2.8	0.056 0.007	0.14 0.018	2,497.5	45	-
	Legs and Feet, Anterior	2.8	0.63 0.041	1.58 0.10	3,515	352	-
	Legs, Posterior	2.8	0.11 ND	0.28 ND	3,515	ND	-
Total							817

Table 2 (Cont.)

Dermal Phosdrin Exposure
to Mixer/Loaders (Excluding Hands)

Worker	Column A Skin Area Studied	Column B Hours of Exposure	Column C Amount of Phosdrin on Cloth Pads (mg/cm ²) Outside Inside Cloth Gauze	Column D Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²) Outside Inside Cloth Gauze	Column E Area of Skin Surface Covered Bare Skin (cm ²)	Column F Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms)	Column G Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
Mixer/ Loader Day 2	Face and Head, Anterior	1.3	0.021 ND	0.11 ND	- 650	- 72	-
	Neck, Anterior	1.3	0.021 ND	0.11 ND	- 160	- 18	-
	Head and Neck, Posterior	1.3	ND ND	ND ND	- 300	- ND	-
	Trunk, Anterior	1.3	0.021 0.005	0.11 ND	3,700 -	ND -	-
	Trunk, Posterior	1.3	ND ND	ND ND	3,330 -	ND -	-
	Arms and Forearms	1.3	0.011 ND	0.059 ND	2,497.5 -	45 -	-
	Legs and Feet, Anterior	1.3	0.17 0.006	0.92 0.032	3,515 -	112 -	-
	Legs, Posterior	1.3	ND ND	ND ND	3,515 -	ND -	-
Total							202

Table 2 (Cont.)

Dermal Phosdrin Exposure
to Mixer/Loaders (Excluding Hands)

Worker	Column A Skin Area Studied	Column B Hours of Exposure	Column C Amount of Phosdrin on Cloth Pads (mg/cm ²) Outside Inside Cloth Gauze	Column D Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²) Outside Inside Cloth Gauze	Column E Area of Skin Surface Covered Bare Skin (cm ²)	Column F Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms) Covered Bare Skin	Column G Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
Mixer/ Loader Day 3	Face and Head, Anterior	1.67	0.47 0.021	1.97 0.088	- 650	- 1,338	-
	Neck, Anterior	1.67	0.47 0.021	1.97 0.088	- 160	- 329	-
	Head and Neck, Posterior	1.67	0.019 ND	0.080 ND	- 300	- 24	-
	Trunk, Anterior	1.67	0.47 0.021	1.97 0.088	3,700 -	326 -	-
	Trunk, Posterior	1.67	0.19 ND	0.080 ND	3,330 -	ND -	-
	Arms and Forearms	1.67	0.062 ND	0.26 ND	2,497.5 -	ND -	-
	Legs and Feet, Anterior	1.67	1.81 0.18	7.59 0.75	3,515 -	2,636 -	-
	Legs, Posterior	1.67	0.073 ND	0.31 ND	3,515 -	ND -	-
Total							4,653

Table 3

Dermal Phosdrin Exposure
to Mixer/Loaders (Excluding Hands)

Worker	Column A Skin Area Studied	Column B Hours of Exposure	Column C Amount of Phosdrin on Cloth Pads (mg/cm ²) Outside Inside Cloth Gauze	Column D Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²) Outside Inside Cloth Gauze	Column E Area of Skin Surface Covered Bare Skin (cm ²)	Column F Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms) Covered Bare Skin	Column G Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
Pilot Day 1	Face and Head, Anterior	2.3	0.025 ND	0.076 ND	- 650	- 49	-
	Neck, Anterior	2.3	0.025 ND	0.076 ND	- 160	- 12	-
	Head and Neck, Posterior	2.3	0.024 ND	0.073 ND	- 300	- 22	-
	Trunk, Anterior	2.3	0.025 ND	0.076 ND	3,700	ND	-
	Trunk, Posterior	2.3	0.024 ND	0.073 ND	3,330	ND	-
	Arms and Forearms	2.3	0.016 ND	0.049 ND	2,497.5	ND	-
	Legs and Feet, Anterior	2.3	0.030 ND	0.091 ND	3,515	ND	-
	Legs, Posterior	2.3	0.029 ND	0.088 ND	3,515	ND	-
Total							83

Table 3 (Cont.)

Dermal Phosdrin Exposure
to Mixer/Loaders (Excluding Hands)

Worker	Column A Skin Area Studied	Column B Hours of Exposure	Column C Amount of Phosdrin on Cloth Pads (mg/cm ²) Outside Inside Cloth Gauze	Column D Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²) Outside Inside Cloth Gauze	Column E Area of Skin Surface Covered Bare Skin (cm ²) Covered Bare Skin	Column F Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms) Covered Bare Skin	Column G Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
Pilot Day 2	Face and Head, Anterior	1.13	0.012 ND	0.074 ND	- 650	- 48	-
	Neck, Anterior	1.13	0.012 ND	0.074 ND	- 160	- 12	-
	Head and Neck, Posterior	1.13	0.013 ND	0.081 ND	- 300	- 24	-
	Trunk, Anterior	1.13	0.012 ND	0.074 ND	3,700	ND	-
	Trunk, Posterior	1.13	0.013 ND	0.081 ND	3,330	ND	-
	Arms and Forearms	1.13	0.006 ND	0.037 ND	2,497.5	ND	-
	Legs and Feet, Anterior	1.13	0.009 ND	0.056 ND	3,515	ND	-
	Legs, Posterior	1.13	0.010 ND	0.062 ND	3,515	ND	-
Total							84

Table 3 (Cont.)

Dermal Phosdrin Exposure
to Mixer/Loaders (Excluding Hands)

Worker	Column A Skin Area Studied	Column B Hours of Exposure	Column C Amount of Phosdrin on Cloth Pads (mg/cm ²) Outside Inside Cloth Gauze	Column D Estimated Phosdrin Exposure Adjusted to 7-Hour Day (mg/cm ²) Outside Inside Cloth Gauze	Column E Area of Skin Surface Covered Bare Skin (cm ²) Covered Bare Skin	Column F Estimated Dermal Phosdrin Exposure for 7-Hour Work Day (Micrograms) Covered Bare Skin	Column G Total Dermal Phosdrin Exposure For Average 7-Hour Work Period (Excluding hands) (Micrograms)
Pilot Day 3	Face and Head, Anterior	1.67	0.005 ND	0.021 ND	- 650	- 14	-
	Neck, Anterior	1.67	0.005 ND	0.021 ND	- 160	- 3	-
	Head and Neck, Posterior	1.67	0.009 ND	0.038 ND	- 300	- 11	-
	Trunk, Anterior	1.67	0.005 ND	0.021 ND	3,700 -	ND -	-
	Trunk, Posterior	1.67	0.009 ND	0.038 ND	3,330 -	ND -	-
	Arms and Forearms	1.67	0.005 ND	0.021 ND	2,497.5 -	ND -	-
	Legs and Feet, Anterior	1.67	0.005 ND	0.021 ND	3,515 -	ND -	-
	Legs, Posterior	1.67	0.009 ND	0.038 ND	3,515 -	ND -	-
Total							28

Table 4

Amount of Phosdrin Found on Hands
of Mixer/Loaders and Pilots

Worker	Column A	Column B	Column C
	Hours of Exposure	Results in Micrograms per Sample	Micrograms Adjusted to 7 Hours of Exposure
Mixer/Loader, Day 1	2.80	42	105
Mixer/Loader, Day 2	1.30	18	97
Mixer/Loader, Day 3	1.67	807	3,383
Pilot, Day 1	2.30	-	89 ^{a/}
Pilot, Day 2	1.13	22	136
Pilot, Day 3	1.67	10	42

^{a/} Estimated Value - calculated by taking average of other pilots.

Table 5

Total Estimated Dermal and Inhalation
Exposure for 7-Hour Work Period

Worker	Estimated Phosdrin Dermal Exposure for Average 7-Hour Exposure (Excluding Hands) (Micrograms)	Estimated Phosdrin Dermal Exposure to the Hands for Average 7-Hour Exposure (Micrograms)	Estimated Phosdrin Inhalation Exposure for Average 7-Hour Work Period (Micrograms)	Total Estimated Phosdrin Exposure During 7-Hour Work Period (Micrograms)
Mixer/Loader, Day 1	799	105	39	943
Mixer/Loader, Day 2	202	97	21	320
Mixer/Loader, Day 3	4,653	3,383	22	8,059
Pilot, Day 1	83	89 ^{a/}	9	181
Pilot, Day 2	84	136	19	239
Pilot, Day 3	28	42	8	78

^{a/} Estimated Value

Appendix 1 - Application Information

	<u>Day 1</u>	<u>Day 2</u>	<u>Day 3</u>
Pesticide used	Phosdrin 4E	Phosdrin 4E	Phosdrin 4E
EPA Reg. No.	07001-00100 AA	07001-00100 AA	07001-00100 AA
Carrier used	Water	Water	Water
Dilution used	1.5 pints/10 gal.	1.5 pints/10 gal.	1 qt./20 gal.
Other chemicals used	Thiosulfan	Thiosulfan	Thiodan, Puregro
Application time (hours)	2.80	1.13	1.67
Beginning temp. (°C)	10	15	10
Ending temp. (°C)	14	20	13
Crop treated	Artichoke	Artichoke	Artichoke

Appendix 2 - Explanation of Calculations Used for the Various Columns of Tables 2 and 3

Below are the methods of calculations used for Tables 2-3:

Column B: Amount of Phosdrin found by analysis in sample

Column C: $\frac{7 \times (\text{Column B})}{\text{Column A}}$

Column D: From Berkow (1931) and DuBois and DuBois (1916)

Column E: (Column C) x (Column D)

Column F: Sum of values from Column E

Appendix 3

Phosdrin Extraction and Analysis Procedures

Extraction of Phosdrin from Cloth Patches

25 ml of acetone was added to the patches (approximately 49 cm²). The sample containers were sealed with aluminum foil and rotated 15 minutes on a jar roller at 30 rpm. Gauze was treated in a similar manner. A portion of the extract was analyzed by gas chromatography without further treatment.

GLC Conditions:

Instrument: Hewlett Packard 5880 with NPD detector at 250° C.

Column: 6 ft. x 2 mm glass packed with 10 % SP-2100 coated on Chromosorb W-HP operating at 160° C. and 35 ml/min. helium carrier gas.

Injector: On column injection, 220° C..

Under these conditions, Phosdrin eluted in 3.25 minutes. There were no interfering materials, and recovery was greater than 95 percent.

Phosdrin in Water Handwashes

Reagents and Equipment:

1. Ethyl acetate, nanograde.
2. Sodium sulfate.
3. 500 ml graduated cylinder.
4. Assorted voumetric glassware and pipets as needed for samples and standards.
5. Gas chromatography:

Instrument: Hewlett Packard 5880 with NPD detector.

Column: 6 ft. x 2 mm glass column containing 10 % SP-2100 coated on 100/120 mesh Chromosorb W-HP operating at 160° C. and 35 ml/min. helium carrier gas.

Temperatures: Detector at 300° C.
Injector at 220° C.

Under these conditions, Phosdrin eluted in about 3.25 minutes.

Analysis:

The amount of solution was measured and recorded. A 100 ml aliquot was placed in a 250 ml separatory funnel. 10 ml saturated NaCl solution was added, and 50 ml ethyl acetate was added for extraction. The water layer was drained, and the ethyl acetate layer was placed in a 100 ml glass-stoppered graduate. The water layer was then reextracted twice with 20 ml ethyl acetate. The extracts were combined in the graduate. The extracts were brought to volume, and sufficient sodium sulfate was added to dry the solvent. Analysis was by GLC.

Recoveries were in excess of 95 percent.

Phosdrin on XAD-4 Air Sample Tubes

Reagents and Equipment:

1. Acetone, nanograde.
2. Analytical grade Phosdrin.
3. Approved and calibrated personal sampling pump.
4. XAD-4 resin tubes, SKC or equivalent.
5. Developing vials with teflon septum caps, SKC #226-02 or equivalent.
6. Tube breaking kit, triangular file, tweezers, paper clip, etc.
7. Assorted volumetric glassware and pipets as needed for standards and samples.
8. Hewlett Packard 5880 gas chromatograph with NPD detector.
9. 6 ft. x 2 mm 10 % SP-2100 on Chromosorb WHP 100/120 mesh glass column.
10. Starting GC parameters with the above column were:
 - a. Injector = 260° C.
 - b. Column = 160° C. and 35 ml/min. helium carrier gas.
 - c. Detector = 300° C.

Analysis:

Interferences: High humidity may affect trapping efficiency.

1. Each sample tube was scored with a file in front of the first section of the resin.

2. Tubes were then broken open.
3. The wire was removed and disposed of.
4. The glass wool, the first (larger) section of resin, and the central foam plug were transferred into a desorption vial containing 3 ml of acetone, and labeled as "front section".
5. The backup portion of the resin was transferred into another desorption vial containing 3 ml of acetone, and labeled as back portion.
6. The desorption vials were then placed on a sample rotator and rotated for 1 hour.
7. The amount of Phosdrin present was determined by gas chromatography.

Determination of Desorption Efficiency:

1. The foam and second (small) portion of resin was removed from an XAD-4 tube of the same lot number to be used for the determinations.
2. A known and reasonable amount (calculated from the amount required to add from the anticipated level of Phosdrin expected in the field or the desired sensitivity) of Phosdrin standard was injected into the remaining section of resin in the tube with a microsyringe. The tube was capped and stored as it would have been during sample shipment. The storage time should be the same as the time expected to elapse between taking the sample and analyzing it.
3. The mean value was determined by running 5 tubes in this manner.
4. Desorption efficiency = $(\text{Area sample} - \text{Area blank}) / (\text{Area standard})$ where the standard is the same amount as injected into the tube.
5. A check on the absorption coefficient was made by following steps 1 and 2 and placing the spiked sample tube on an air pump and drawing a representative volume of air through the tube at a representative sampling rate before storage. This determination is much easier when leaving the back portion of resin in the tube.

Calculations:

1. The weight of Phosdrin present on tube section was determined by gas chromatographic analysis in nanograms.
2. Total weight was corrected by subtracting any weight value from the blank or control tube.
3. The corrected weight was divided by the determined desorption efficiency (and adsorption efficiency if needed) to obtain the final corrected weight of Phosdrin present.

4. The volume of air sampled was converted to stand conditions of 25° C. and 760 mm Hg.

$$VS = (V \times P \times 298) / (760 \times [T + 273])$$

where:

VS = volume of air at STP
V = volume of air as measured
P = barometric pressure in mm Hg
T = temperature of the air in degrees Centigrade.

5. Ppb vapor phase in the air was calculated from the above data.

$$\text{ppb v/v} = (ns \times 24.45) / (VS \times 224)$$

where:

ns = corrected nanograms (3#)
VS = corrected air volume in liters (#4)
224 = molecular weight of Phosdrin.

for Phosdrin at 25° C.,

$$\text{ppb v/v} = (ns \times 0.10915) / VS.$$